Domain Patterns, Texture and Macroscopic Electro-mechanical Behavior of Ferroelectrics

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Abstract. This paper examines the domain patterns and its relation to the macroscopic electromechanical behavior of ferroelectric solids using a theory based on homogenization and energy minimization. The domain patterns in different crystalline systems are classified, the spontaneous strain and polarization for single crystals and polycrystals are characterized, and the optimal texture of polycrystals for high-strain actuation is identified. The results also reveal why it is easy to pole PZT at compositions close to the 'morphotropic phase boundary'.

INTRODUCTION

Ferroelectric solids are widely used in transducers applications based on their piezoelectricity. The strains they display, however, are quite small, and there have been many attempts to find methods to increase them. These efforts received a significant boost when Shrout and Park [1] demonstrated strains as large as 1.7% through electrostriction of a single-crystal relaxor ferroelectric PMn-Pt. There have also been significant advances towards a fundamental understanding of the electromechanical properties of ferroelectrics. In particular, there has been much progress at the quantum mechanical level in both hard and relaxor ferroelectrics, and at the cluster level in relaxors.

This paper reports on some recent theoretical and experimental work on hard ferroelectric materials. These materials form complicated domain patterns, which can be changed through the application of an external electric field and mechanical stress. The change in domain pattern, however, may involve a significant change in polarization and strain, and lead to significant mismatch between grains in polycrystals. Therefore, inter-granular constraints severely restrict possible changes in domain patterns in polycrystals. Even in single crystals, the changes can lead to mismatch with the loading device and may consequently be suppressed. Therefore one requires very large forces and fields for switching domain patterns, and such switching is often accompanied by mechanical and electrical damage. Therefore, the use of hard ferroelectrics is often limited to those regimes where the domains are stationary. There are exceptions as during poling or in more recent memory devices.

The domain patterns also pose a challenge to a complete theoretical understanding of the macroscopic behavior of hard ferroelectrics, as they occur at a length and time scale which is inaccessible to both the classical macroscopic theories and the modern

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ab initio methods and effective Hamiltonians. In other words, they are sufficiently complicated and influential to be ignored, yet their interactions are sufficiently complex that studying a few unit cells or one wall does not reveal the entirity of their behavior. This paper reports on an attempt to understand these intermediate scales. It begins with a classical and phenomenological Landau-Ginzburg-Devonshire type theory, shows that this theory reveals important aspects of domain patterns, and tries to systematically average their effect to larger scales. It reports on the work of Shu and Bhattacharya [2] and Burscu, Ravichandran and Bhattacharya [3] on single crystals and then summarizes the work of Li and Bhattacharya [4] on polycrystals. This line of research parallels recent work in the study of the shape-memory effect in martensitic materials [5-8], and magnetostriction in the recently developed ferromagnetic shape-memory alloys [9,10]. In particular, this work adapts the constrained theory of magnetostriction of DeSimone and James [10] to ferroelectrics and extends it to polycrystalline media following Bhattacharya and Kohn [6].

THEORETICAL FRAMEWORK

Electroelastic Energy

Consider a ferroelectric crystal Ω subject to an applied traction $\mathbf{t}_0$ on part of its boundary $\partial_2\Omega$ and external applied electric field $\mathbf{E}_0$. The displacement $\mathbf{u}$ and polarization $\mathbf{p}$ of the ferroelectric are those that minimize the potential energy

$$\int_{\Omega} \frac{1}{2}\nabla\mathbf{p}\cdot\mathbf{A}\nabla\mathbf{p} + W(\mathbf{x},\mathbf{e}[\mathbf{u}],\mathbf{p}) - \mathbf{E}_0\cdot\mathbf{p}\,d\mathbf{x} - \int_{\partial_2\Omega}\mathbf{t}_0\cdot\mathbf{u}\,dS + \int_{R^3}\frac{\varepsilon_0}{2}|\nabla\phi|^2\,d\mathbf{x}\,. \qquad (1)$$

Above, $\mathbf{A}$ is a positive-definite matrix so that the first term above penalizes sharp changes in the polarization, and may be regarded as the energetic cost of forming domain walls. The second term W is the stored energy density (Landau energy density) which depends on the state variables or order parameters, strain $\mathbf{e}$ and polarization $\mathbf{p}$, and also explicitly on position $\mathbf{x}$ in polycrystals and heterogeneous media. W encodes all the crystallographic and texture information, and is discussed in more detail below. The third term is the potential associated with the applied electric field, while the fourth term is the potential energy associated with the applied mechanical load. The final term is the electrostatic field energy that is generated by the polarization distribution. For any polarization distribution, the electrostatic potential ϕ is determined by solving Maxwell equation in all space subject to appropriate boundary conditions. Thus, this last term is a non-local. This potential is essentially one used in the classical Landau-Ginzburg-Devonshire theory, except the electrostatic contribution to energy is accounted for with some care.

Ferroelectric crystals are non-polar above the Curie temperature with a preferred lattice structure, but are spontaneously polarized below the Curie temperature with a spontaneous strain. Further, because of a change in symmetry, they can be spontaneously polarized and strained in one of K crystallographically equivalent variants. Thus, if $\mathbf{e}^{(i)}$ is the spontaneous strain and $\mathbf{p}^{(i)}$ is the spontaneous

polarization of the *i*th variant ($i = 1, ..., K$), then the stored energy W is minimum (zero without loss of generality) on the $\mathbf{Z} = \bigcup_{i=1}^{K} \{(\mathbf{e}^{(i)}, \mathbf{p}^{(i)})\}$ and grows away from it. In other words it has a multi-well structure with wells $\mathbf{Z}$. Finally note that in a polycrystalline medium, if $\mathbf{R}(\mathbf{x})$ denotes the rotation that maps the crystallographic frame to a reference frame, then $W(\mathbf{x},\mathbf{e},\mathbf{p}) = W_0(\mathbf{R}(\mathbf{x})\mathbf{e}\mathbf{R}^{\mathbf{T}}(\mathbf{x}), \mathbf{R}(\mathbf{x})\mathbf{p})$ where W_0 is the energy density of a reference crystal.

Since W has a multi-well structure, minimization of the potential energy in Eq. (1) leads to domain patterns or regions of almost constant strain and polarization close to the spontaneous values separated by domain walls. However, the solutions are rather complicated [11] as one has to resolve the length scales determined by the domain wall energy (square-root of smallest eigen-value of $\mathbf{A}$), and yet one has multiple domains in the setting of current interest where the specimen Ω is large compared to the domain wall thickness. In this setting, however, the domain wall energy has a negligible effect on the macroscopic behavior and may thus be dropped [12]. This leads to an ill-posed problem as the minimizers develop oscillations at a very fine scale, however there has been significant recent progress in studying such problems. Therefore $\mathbf{A}$=0 in what follows.

Homogenization

Now consider a ferroelectric polycrystal with numerous small grains. Each grain in turn forms numerous domains as shown in Fig. 1. The functional (1) (with $\mathbf{A}$=0) describes all the details of the domain pattern in each grain, and thus is rather difficult to understand. It would be very useful to obtain a functional that directly captures the *effective* macroscopic behavior of all the domains and grains without describing all the details. The theory of Γ-convergence introduced by De Giorgi [13,14] provides us a framework to derive such an effective or homogenized theory.

Suppose the texture of polycrystal is periodic with period $\varepsilon > 0$, i.e., suppose that $W(\mathbf{x},\mathbf{e},\mathbf{p})$ be a periodic function of $\mathbf{x}$ with period ε. Then, as $\varepsilon \to 0$, the effective behavior of the polycrystal is described by the functional

$$\int_{\Omega} \frac{1}{2} \nabla \mathbf{p} \cdot \mathbf{A} \nabla \mathbf{p} + \overline{W}(\mathbf{e}[\mathbf{u}], \mathbf{p}) - \mathbf{E}_0 \cdot \mathbf{p} d\mathbf{x} - \int_{\partial_2 \Omega} \mathbf{t}_0 \cdot \mathbf{u} dS + \int_{R^3} \frac{\varepsilon_0}{2} |\nabla \phi|^2 \, d\mathbf{x} \qquad (2)$$

in the sense that the minimizers of the functional (2) approximate in an appropriate sense [4] those of functional (1). Notice that the spatially heterogeneous energy density W in (1) replaced with a spatially homogeneous energy density $\overline{W}$ in (2). $\overline{W}$ is the *effective energy density* of the polycrystal, and can be obtained by solving the following variational problem on an unit cell:

$$\overline{W}(\mathbf{e},\mathbf{p}) = \inf_{k} \inf_{\mathbf{u}' \in H^1_{Per}(kY)} \inf_{\mathbf{p}' \in L^2(kY)} \frac{1}{|kQ|} \int_{kQ} \left\{ W(\mathbf{y}, \mathbf{e} + \nabla \mathbf{u}', \mathbf{p} + \mathbf{p}') + \frac{\varepsilon_0}{2} |\nabla \phi'|^2 \right\} d\mathbf{y} \, . \qquad (3)$$

It turns out that in this formula (3) above, one may replace W with a relaxed or mesoscale energy $\hat{W}$ which may be defined for each $\mathbf{y}$ by holding it constant in the formula (3). $\hat{W}$ is the *effective energy density* of the single crystal.

These ideas are illustrated in Fig. 1. The energy density W describes the behavior at the smallest length-scale. It has a multi-well structure as discussed earlier. This leads to domains, and $\hat{W}(\mathbf{x},\mathbf{e},\mathbf{p})$ is the energy density of the grain at $\mathbf{x}$ after it has formed a domain pattern with average strain $\mathbf{e}$ and average polarization $\mathbf{p}$. Note that this energy is zero on a set $\mathbf{Z}^S$ which is larger than the set $\mathbf{Z}$. $\mathbf{Z}^S$ is the set of all possible *average spontaneous strains and polarizations* that a single crystal can have by forming domain patterns. But $\hat{W}$ and $\mathbf{Z}^S$ can vary from grain to grain. The collective behavior of the polycrystal is described by the energy density $\overline{W}$. $\overline{W}(\mathbf{e},\mathbf{p})$ is the energy density of a polycrystal with grains and domain patterns when the average strain is $\mathbf{e}$ and the average polarization is $\mathbf{p}$. Notice that it is zero on the set $\mathbf{Z}^P$ which describes the set of all possible average spontaneous strains and polarization of the polycrystal.

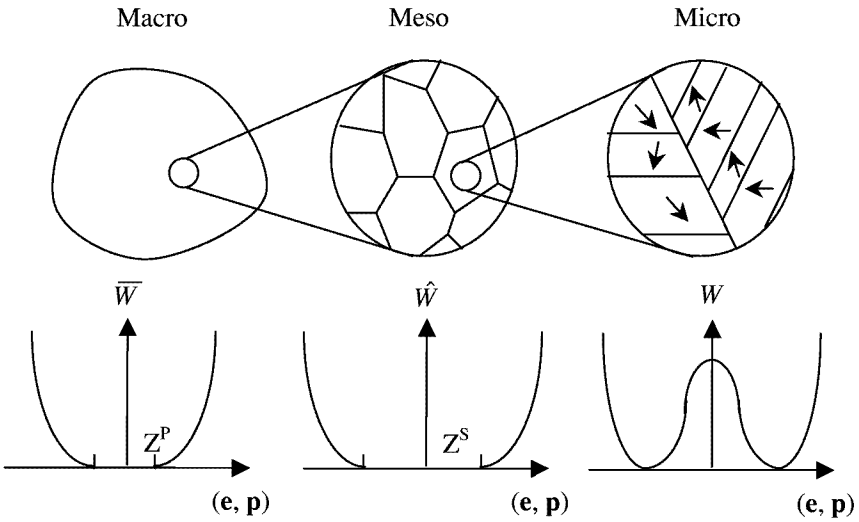

Figure 1. The multi-well structure of stored energy density W, the effective energy density of a single crystal $\hat{W}$, and the effective energy density of a polycrystal $\overline{W}$.

SINGLE CYRSTALS

Domain Patterns

The multi-well structure of the stored energy density W gives rise to minimizers that consist of domains of differently oriented polarization separated by domain walls. In order to form a domain wall between variants i and j, i.e., to find an interface separating regions of strains and polarization $(\mathbf{e}^{(i)}, \mathbf{p}^{(i)})$ and $(\mathbf{e}^{(j)}, \mathbf{p}^{(j)})$, in an energy

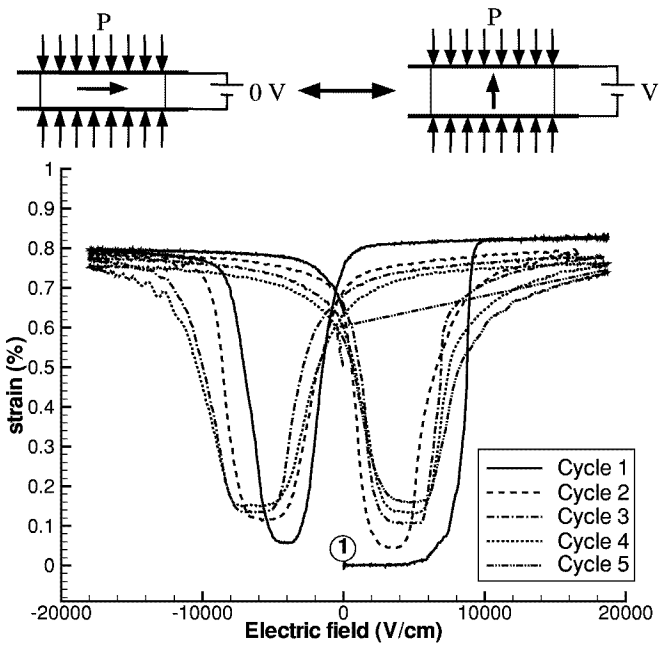

Figure 2. A single crystal of Barium Titanate with <001> orientation subjected to constant compressive stress and cyclic electric field displays very large electrostriction [3].

minimizing manner, it is necessary and sufficient to satisfy two compatibility conditions [2]:

$$\mathbf{e}^{(j)} - \mathbf{e}^{(k)} = \frac{1}{2}(\mathbf{a} \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{a}), \qquad (\mathbf{p}^{(j)} - \mathbf{p}^{(k)}) \cdot \mathbf{n} = 0, \tag{4}$$

where $\mathbf{n}$ is the normal to the interface, $\mathbf{a}$ is the shear across the domain wall and $\mathbf{a} \otimes \mathbf{n}$ denotes the matrix with components $a_i n_j$. The first is the mechanical compatibility condition which assures the mechanical integrity of the interface, and the second the electrical compatibility conditions which assures that the interface is uncharged and thus energy minimizing. Given $(\mathbf{e}^{(j)}, \mathbf{p}^{(j)})$ and $(\mathbf{e}^{(i)}, \mathbf{p}^{(i)})$, we need to solve these equations for vectors $\mathbf{a}$ and $\mathbf{n}$. At first glance it appears impossible to solve these equations simultaneously: the first equation has at most two solutions for the vectors $\mathbf{a}$ and $\mathbf{n}$, and there is no a priori reason that these values of $\mathbf{n}$ will satisfy the second. It turns out however, that if the variants are related by two-fold symmetry, i.e.,

$$\mathbf{e}^{(j)} = \mathbf{R}\mathbf{e}^{(k)}\mathbf{R}^{\mathrm{T}}, \qquad \mathbf{p}^{(j)} = \mathbf{R}\mathbf{p}^{(k)}, \tag{5}$$

for some 180° rotation $\mathbf{R}$, then it is indeed possible to simultaneously solve the two equations in (4) [2,10].

Shu and Bhattacharya [2] studied the domains walls in materials that are cubic above Curie temperature and either $<001>_c$ polarized tetragonal, $<111>_c$ polarized rhombohedral, $<110>_c$ polarized orthorhombic, or $<a11>_c$ polarized monoclinic. The

only domain walls in the tetragonal phase are 180° and 90° domain walls, and the 90° domain walls have a structure similar to that of compound twins with a rational $\{110\}_c$ interface and a rational $<110>_c$ shear direction. The only possible domain walls in the orthorhombic phase are 180° domain walls, 90° domain walls having a structure like that of compound twins with a rational $\{100\}_c$ interface, 120° domain walls having a structure like that of type I twins with a rational $\{110\}_c$ interface and 60° domain walls having a structure like that of type II twins with an irrational normal. The only possible domain walls in the rhombohedral phase are the 180° domain walls, and the 70° or 109° domain walls with a structure similar to that of compound twins. They also studied more complex patterns involving layers within layers.

Finally, they used the theory to motivate a configuration to obtain large electrostriction using tetragonal materials. This was subsequently confirmed experimentally by Burcsu et al. [3] as shown in Fig. 2. A single crystal in the shape of a flat plate of a tetragonal material with $<001>_c$ orientation with electrodes on top and bottom faces is subjected to a constant compressive load and a cyclic voltage. The polarization then cycles between two states, resulting in a strain close to the c/a ratio of the material. The experimental set-up allows in-situ observation and confirms that the switching from one state to another is mediated by domain walls sweeping across the specimen [15].

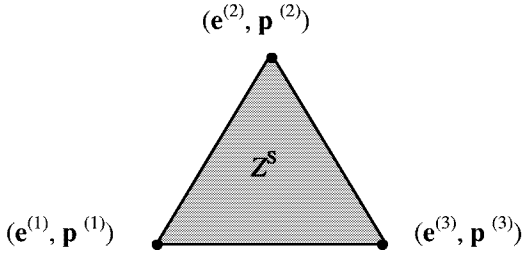

Figure 3. The set of average spontaneous strain and polarization of a single crystal.

Average Spontaneous Strain and Polarization of a Single Crystal

As the single crystal forms domain patterns, its overall behavior is described by the energy density $\hat{W}$ and the possible average spontaneous strain and polarization is given by the set $\mathbf{Z}^S$. The following result allows the characterization of this set. Suppose the ferroelectric material has $K = 2n$ variants, and suppose further that each pair of variants is compatible (each pair satisfies Eq. (4) for some vectors **a**, **n**). Then, $\mathbf{Z}^S$ is given by all possible averages of spontaneous strains and polarizations [4,10]:

$$\mathbf{Z}^S = \left\{ (\mathbf{e},\mathbf{p}) : \mathbf{e} = \sum_{i=1}^{n} \lambda_i \mathbf{e}^{(i)}, \quad \mathbf{p} = \sum_{i=1}^{n} \lambda_i (2f_i - 1)\mathbf{p}^{(i)}, \quad \lambda_i \geq 0, \sum_{i=1}^{n} \lambda_i = 1, \quad 0 \leq f_i \leq 1 \right\}. \quad (6)$$

In other words, if each pair of variants is compatible, then compatibility poses no restriction, and it is possible to find energy minimizing and compatible domain pattern for any arbitrary average. This is shown schematically in Fig. 3.

Tetragonal Phase

The spontaneous strains and polarization of tetragonal ferroelectric are of the form

$$\mathbf{e}^{(1)} = \mathrm{diag}[\beta, \alpha, \alpha], \quad \mathbf{p}^{(1)} = [p, 0, 0], \tag{7}$$

and their symmetry-related variants. The total number of variants is 6, and each pair is compatible so that one can use Eq. (6). One can readily see that the average spontaneous strains of single crystal have fixed trace $2\alpha + \beta$ and zero off-diagonal elements. Consequently these strains lie in a 2-dimensional subspace of the 5-dimensional linear space of deviatoric (shear-like) strains.

Rhombohedral Phase

Here one has eight variants, and again all pairs are compatible so that Eq. (6) holds. The average spontaneous strains lie in a 3-dimensional subspace of the 5-dimensional linear space of deviatoric strains.

Tetragonal-Rhombohedral Phase Co-Existence

Suppose one has a material where both the tetragonal and rhombohedral phases can coexist. Then one has both sets of wells. While the tetragonal variants are all pair-wise compatible amongst themselves, and the rhombohedral variants are all pair-wise compatible amongst themselves, a tetragonal variant is compatible with a rhombohedral variant if and only if the spontaneous strains and polarization satisfy a very special relationship. Thus, it is not possible, in general, to apply Eq. (6). It is possible however to estimate the set $\mathbf{Z}^S$ from inside, and use this inner (conservative) estimate to show that $\mathbf{Z}^S$ spans the 5-dimensional deviatoric strain space and 3-dimensional polarization space [4]. Thus, crystals with Tetragonal-Rhombohedral phase co-existence have a full dimensional set $\mathbf{Z}^S$ in contrast to either Tetragonal or Rhombohedral alone. This will have important consequences later.

Monoclinic Phase

In a monoclinic phase, not all pairs of variants are compatible in general and it is not possible to use Eq. (6). It is possible however to estimate the set $\mathbf{Z}^S$ from inside, and use this inner (conservative) estimate to show that $\mathbf{Z}^S$ spans the 5-dimensional deviatoric strain space and 3-dimensional polarization space [4]. Thus, crystals with a monoclinic phase also has a full dimensional set $\mathbf{Z}^S$. This will have important consequences later.

POLYCRYSTALS

A polycrystal is a collection of perfectly bonded single crystal with large number of distinct orientations. Its overall behavior is described by the energy density $\overline{W}$, and possible values of average spontaneous strain and polarization is given by the set $\mathbf{Z}^P$.

$\mathbf{Z}^P$ is the set of all strains and polarizations that can be obtained as macroscopic averages of locally varying strain and polarization fields which is stress and depolarization field free. In other words, they are accommodated within each grain by rearrangement of ferroelectric variants, and satisfy the compatibility condition at the grain boundary. Therefore the size of the set $\mathbf{Z}^P$ is an estimate of the ease with which a ferroelectric polycrystal may be poled, and also the strains that one can expect through domain switching.

Recall that the energy density $\overline{W}$ is defined through a difficult variational problem, and thus very difficult to evaluate explicitly. The set $\mathbf{Z}^P$ is also similarly difficult to evaluate. Therefore it is necessary to understand their behavior using bounds.

Taylor Bound

One can obtain a very simple upper bound on the energy $\overline{W}$, and inner bound on the set $\mathbf{Z}^P$ by assuming that the strain and polarization is constant in each grain. This is referred to as the Taylor bound in analogy to plasticity. This bound has a very simple geometric interpretation as shown in Fig. 4. The Taylor bound $\mathbf{Z}^T$ is simply the intersection of all possible sets $\mathbf{Z}^S(\mathbf{x})$ corresponding to the different grains as $\mathbf{x}$ varies over the entire crystal.

$$\mathbf{Z}^P \supseteq \mathbf{Z}^T = \bigcap_{\mathbf{x}\in\Omega} \mathbf{Z}^S(\mathbf{x}) = \left\{(\mathbf{e},\mathbf{p}) \;\middle|\; (\mathbf{R}(\mathbf{x})\mathbf{e}\mathbf{R}^T(\mathbf{x}), \mathbf{R}(\mathbf{x})\mathbf{p}) \in \mathbf{Z}^S(\mathbf{x}), \forall \mathbf{x} \in \Omega\right\}. \qquad (8)$$

As we can see, the calculation of Taylor bound depends on the polycrystal texture. It turns out that this simple bound is a surprisingly good indicator of the actual behavior of the material.

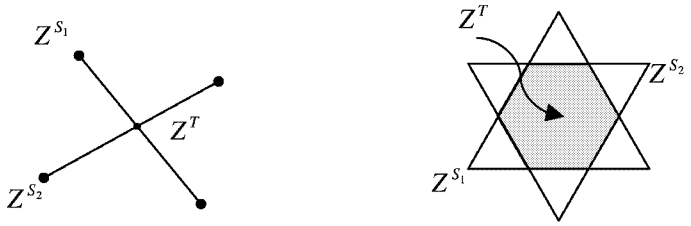

Figure 4. Taylor bound as the intersection of the set of average spontaneous strain and polarizations associated with the different grains.

Tetragonal Phase

Recall that for a tetragonal ferroelectric, the set $\mathbf{Z}^S$ contains strains with only diagonal elements. Thus, the intersection of these sets corresponding to different orientation is as shown on the left in Fig. 4, and leads to a set $\mathbf{Z}^T$ with a single point unless the orientations of the grains are limited to having a common $<001>_c$ axis. In other words, if a polycrystal does not have a strong $<001>_c$ texture, the intergranular constrains will be so strong as to prevent any macroscopic average spontaneous strain or polarization. Such a polycrystal would be very difficult to pole, and will show no

macroscopic strain through domain switching. Therefore, it is necessary to have a polycrystal with a $<001>_c$ texture if one were to pole this material, or to use it for large strains through domain switching.

Rhombohedral Phase

The rhombohedral phase is very similar to the tetragonal. Once again, a general polycrystal is difficult to pole, and would show no macroscopic strain through domain switching. It is necessary to have a polycrystal with $<111>_c$ fiber texture if one were to pole this material, or to use it for large strains through domain switching.

Tetragonal-Rhombohedral Phase Co-Existence

Recall that when the tetragonal and rhombohedral phases co-exist, then the set of average spontaneous strains and polarizations has full dimension. So the calculation of the Taylor bound is as shown on the right of Fig. 4. The polycrystal, irrespective of texture, has a significant set of macroscopic average strains and polarizations. Thus, this would be a material which would be easy to pole. Further domain switching could be affected in these materials with limited inter-granular constrains.

Monoclinic Phase

Recall that for a monoclinic phase, as in the case just above, the set of average spontaneous strains and polarizations has full dimension. So the calculation of the Taylor bound is as shown on the right of Fig. 4. The polycrystal, irrespective of texture, has a significant set of macroscopic average strains and polarizations. Thus, this would be a material which would be easy to pole. Further domain switching could be affected in these materials with limited inter-granular constrains.

Implications

The preceding analysis shows that for a material which is cubic above Curie temperature, and $<001>_c$ polarized tetragonal below it, it is necessary to have polycrystals with a $<001>_c$ fiber texture in order to be able to pole it or to affect any domain switching. Similarly a $<111>_c$ polarized rhombohedral material requires $<111>_c$ fiber texture. In contrast, in materials with tetragonal-rhombohedral phase co-existence, or in materials with a monoclinic phase, one has some average spontaneous strain and polarization irrespective of texture.

The commonly use piezoelectric material PZT ($Pb(Zr_xTi_{1-x})O_3$) is a solid solution of Lead Titanate and Lead Zirconate. It is rhombohedral in the Zirconium rich compositions, and tetragonal in the Titanium rich compositions. It has a morphotropic phase boundary at around $x = 0.52$ where it was believed that the tetragonal and rhombohedral phases coexist but it has recently been learnt that the material is monoclinic at this composition [16,17]. It has also long been known that PZT is very difficult to pole in the Titanium rich tetragonal compositions, and the Zirconium rich rhombohedral compositions, but relatively easy to pole at the morphotropic boundary.

The preceding analysis provides an explanation, as the set $\mathbf{Z}^T$ is trivial in the tetragonal and the rhombohedral states, but large when one has tetragonal-rhombohedral co-existence or a monoclinic phase. In other words, the intergranular constrains were extremely high and prevented any macroscopic average spontaneous strain in the tetragonal or rhombohedral compositions, but not significant to prevent macroscopic average spontaneous strain and polarization at the morphotropic phase boundary.

CONCLUSIONS

This paper has summarized a line of research aimed at understanding domain patterns, and its relation to the macroscopic electro-mechanical properties. The domain patterns in different crystalline systems have been classified, large electrostrictive strains through domain switching has been demonstrated, the average spontaneous strain and polarization for single crystals and polycrystals have been characterized, and the optimal texture of polycrystals for high-strain actuation have been identified. The results also explain why it is easy to pole PZT at compositions close to the morphotropic phase boundary.

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